RESPONSE OF THE PLASTIC LAKE CATCHMENT, ONTARIO, TO REDUCE SULPHUR DEPOSITION

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RESPONSE OF THE PLASTIC LAKE CATCHMENT, ONTARIO, TO REDUCED SULPHUR DEPOSITION

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PREFACE

This report was produced as a result of the ongoing Acidic Precipitation in Ontario Study and forms the substance of a presentation given at the International Conference on Acidic Deposition in Glasgow from September 16 to 21, 1990. The report discusses the effects of decreased sulphate deposition on the chemistry of streamwater draining the Plastic lake catchment.

ABSTRACT

The atmospheric deposition rate of sulphur in eastern North America has decreased in the last 10-15 years (Hedin et al. 1987, Dillon et al. 1988). In central Ontario, Canada, a decline of 35-40% occurred with a mean change in annual average concentration of sulphate in precipitation of ~ 4 μeq L^{-1} yr^{-1} averaged over the period 1976-85. The decline in H^+ concentration (calculated from pH) was of comparable magnitude (3.3 μeq L^{-1} yr^{-1}), while the concentration of either the nitrogen species (nitrate, ammonium ion) or base cations (calcium, magnesium, sodium and potassium) in precipitation remained unchanged. At the same time a lake that we have monitored since 1979, Plastic Lake, has acidified (Dillon et al. 1987), with alkalinity dropping an average of 2 μeq L^{-1} yr^{-1} between 1979 and 1985. Simultaneously, total base cations ($C_b = Ca^{2+} + Mg^{2+} + Na^+ + K^+$) decreased in the lake while SO_4^{2-} did not change significantly. Extensive studies of the tributaries and of the catchment of Plastic Lake have also been conducted. In this paper, we describe the effects of the decrease in SO_4^{2-} deposition on the chemistry of streamwater draining the Plastic Lake catchment. Water quality of runoff from an upland site improved rapidly (pH and alkalinity increased, SO_4^{2-} and Al decreased), but two factors negated these improvements. A small wetland area downstream reversed most of these changes, resulting in a constant output of strong acid from the catchment. In addition, in extremely dry years (1983, 1987) there were very high concentrations of SO_4^{2-} in the streamwater, suggesting substantial re-oxidation of reduced S in the catchment. We attempt to explain the acidification of the lake in view of these changes within the catchment.

RÉSUMÉ

Le taux de dépôt atmosphérique du soufre dans l'est de l'Amérique du Nord a diminué au cours des 10-15 dernières années[1,2]. Dans le centre de l'Ontario, au Canada, une baisse de 35-40% s'est produite, avec un changement moyen annuel de la concentration de sulfates dan les précipitations de ~ 4 μeq L^{-1} an^{-1}, calculé sur la période 1976-85. Le déclin dans la concentration H^+ (calculé à partir du pH) était d'une ampleur comparable (3.3 μeq L^{-1} an^{-1}), tandis que la concentration de l'une ou l'autre des espèces d'azote (nitrate, ion d'ammonium) ou de cations de bases (calcium, magnésium, sodium et potassium) restait inchangée dans les précipitations. Au même moment, un lac que nous étudions depuis 1979, le lac Plastic, s'est acidifiéd, son alcalinité diminuant d'une moyenne de 2 μeq L^{-1} an^{-1} entre 1979 et 1985. Simultanément, le total des cations de bases ($C_b = Ca^{2+} + Mg^{2+} + Na^+ + K^+$) a diminué dans le lac, alors que le SO_4^{2-} n'a pas changé de façon sig··ificative. Des études approfondies des affluents et de la surface de captation du lac Plastic ont aussi été menées. Dans cet exposé, nous décrivons les effets d'une diminution dans les dépots de SO_4^{2-} sur la chimie de l'au s'écoulant de la surface de captation du lac Plastic. La qualité du ruissellement d'un site en amont s'est améliore rapidement (le pH et l'alcalinité le SO_4^{2-} et l'Al ont diminué), mais deux facteurs annulèrent ces améliorations. Une petite zone marécageuse en aval renversa la plupart de ces changements, résultant en un flot constant d'acide puissant provenant de la surface de captation. De plus, lors d'années extrêmement sèches (1983, 1987), il y avait de très hautes concentrations de SO_4^{2-} dans le cours d'eau, suggérant une ré-oxydation substantielle du S réduit dans la surface de captation. Nous tentons d'expliquer l'acidification du lac en tenant compte de ces changements dans la surface de captation.

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Table 2. Initial concentration (average of first 6 months) and rate of change of chemical parameters (μeq L^{-1} yr^{-1} except pH or unless otherwise specified) in main inflow to Plastic Lake (PC1). Results are based on linear regression analysis of monthly average concentrations vs. month number for the period May 1979 to December 1987. Between 1 and 119 samples per month were collected depending on flow volume. C_b is the sum of base cations (= Ca^{2+} + Mg^{2+} + Na^+ + K^+), s.e. is standard error, r is correlation coefficient, p (probability of r) is denoted as: $p < 0.05$ = *, $p < 0.001$ = **, $p < 0.00001$ = ***, NS = not significant. Al and F concentrations are totals of all chemical species.

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Fig. 1 Map of Plastic Lake subcatchment 1 showing location of wetland areas and sampling stations.

Fig. 2 Monthly average concentrations of alkalinity, SO_4^{2-} and base cations (C_b at (a) sites above all wetland influence (PC1-108) and (b) at the base of the catchment (PC1).

INTRODUCTION

Plastic Lake's catchment (88.6 ha) is drained by 7 small streams, 6 of which are ephemeral. The largest (22.3 ha) of the 7, subcatchment #1 (PC1; Fig. 1), flows year-round except in very dry years. Five of the 7 inflow subcatchments including PC1 drain wetlands (Sphagnum-conifer swamps or shallow beaver ponds) while the smallest 2 are soil-water seeps that flow only in spring and fall. The chemistry of the 5 inflows draining wetlands is very similar (LaZerte et al. 1984). Only PC1 has been extensively sampled and is discussed here.

The PC1 catchment (Fig. 1) is underlain by biotite gneiss with pegmatitic veins. There is some amphibolite bedrock present in low-lying areas beneath the soil cover. The dominant soil minerals are quartz (30%), plagioclose feldspar (30%), and potassium feldspar (15%), with lesser amounts of vermiculite, amphibole and goethite (Kirkwood et al. 1989). The soil cover is very thin, averaging about 0.5 m (about 0.3 m in the portion of the catchment upstream of the wetland) with bedrock outcrops comprising 10% of the area. The soils are weakly-developed orthic humo-ferric and ferro-humic podzols, with humic mesisols under the Sphagnum-conifer swamp. The majority of soil profiles have no C horizon. The cation exchange capacity of the podzols averages about 17 meq/100 g, with base saturation of approximately 30% (Lorzano 1987, Neary et al. 1987).

METHODS

Samples were collected for chemical analyses at site PC1 at the bottom of the catchment from May, 1979 and at site PC1-08 above the Sphagnum-conifer swamp (Fig. 1) from November, 1982. The number of samples collected averaged 9 and 7 per month at PC1 and PC1-08, respectively. The field sampling methods, hydrologic and analytical methods are described in detail elsewhere (Ont. Min. 1983, Scheider et al. 1983, Locke et al. 1985). Organic acid anion concentrations (A^-) were calculated from dissolved organic carbon (DOC) and pH according to the method described by Oliver et al. (Oliver et al. 1983) and validated previously (LaZerte et al. 1984) for the Plastic Lake catchment. Chemical concentrations were averaged (not flow-weighted) to produce mean monthly values, and long-term trends evaluated by linear regression of concentrations vs. month number.

RESULTS AND DISCUSSION

The decline in SO_4^{2-} (and H^+) concentration in precipitation reported for 1976-85 did not continue in subsequent years; in fact, the decrease from about 90 μeq L^{-1} in 1976 to 55 μeq L^{-1} in 1983 was followed by a period of 6 years where SO_4^{2-} concentration was constant (55 ± 5 μeq L^{-1}). Thus, the long-term pattern in deposition chemistry can be described as a 7-year period with decreasing SO_4^{2-} and H^+ followed by a 6-year period with constant concentrations (and deposition rates).

The decline in SO_4^{2-} deposition in eastern North America resulted in a decrease in SO_4^{2-} concentration in some lakes (Dillon et al. 1987, Kelso et al. 1988), and streams (Lins 1986, Smith et al. 1983). For example, in Harp Lake, 30 km from Plastic Lake, SO_4^{2-} decreased by 4 $\mu eq\ L^{-1}\ yr^{-1}$ between 1979 and 1987[3], and its 6 tributary streams' SO_4^{2-} concentrations decreased by 5-7 $\mu eq\ L^{-1}\ yr^{-1}$. These decreases were offset by changes in base cation concentrations. The thick glacially-deposited overburden in the Harp Lake catchment was responsible for the fact that, unlike Plastic Lake, acidification was not occurring in Harp Lake; thus, the decline in SO_4^{2-} deposition was not manifested as an increase in pH or alkalinity.

The monthly average concentrations of alkalinity, SO_4^{2-} and C_b at PC1 and PC1-08 are shown in Fig. 2. Inspection of the figures clearly indicates that substantial changes in the chemistry of the two sites occurred from the initiation of the study to 1987. Very high concentrations of SO_4^{2-} (as well as low alkalinity and pH, and high C_b) were observed in the fall period of 1983 and especially 1987, immediately following the only extensively dry periods during the study. There are also obvious seasonal patterns in these parameters, but we focus our attention here on long-term changes. Improvements in water quality at PC1-08 (higher alkalinity, lower SO_4^{2-}) stopped at about the end of 1987, possibly as a delayed response to the constant SO_4^{2-} deposition. In this paper, we consider only the period where water quality improved, i.e. to the end of 1987.

Rates of changes of the chemistry of the water draining the upland part of the catchment (PC1-08) are shown in Table 1. Acid neutralizing capacity (measured as alkalinity) increased very substantially, by 4.6 $\mu eq\ L^{-1}\ yr^{-1}$ from negative values (~ -10 μeq

L^{-1}) indicating the presence of an excess of strong acid, to positive values (~ +12 μeq L^{-1} yr^{-1}). Concurrently, pH increased from ~ 4.8 to ~ 5.0, and sulphate, the mobile anion associated with the transport of protons (Reuss et al. 1985), decreased rapidly (-6.3 μeq L^{-1} yr^{-1}). There was also a slight change in Cl (-1.0 μeq L^{-1} yr^{-1}) but no change in DOC or organic anions. The total decrease in acid anions (-7.3 μeq L^{-1} yr^{-1}) was partly offset by the decrease in alkalinity, but also by the decrease in aluminium (Table 3). Total aluminum declined by 45 μg L^{-1} yr^{-1}, from approximately 600 μg L^{-1} at the start of the study to 350 μg L^{-1} by 1987; speciation (Lazerte 1989) showed that only the inorganic monomeric fraction which typically made up ~ 90% of the total decreased. Similarly, speciation calculations showed that almost all the F in PC1-08 was present as Al-F complexes, so the decrease in F (-0.3 μeq L^{-1} yr^{-1}) is expected. If the average charge on the Al species is +2 (Dillon et al. 1988), then this change corresponds to an equivalent decline of -3.3 μeq L^{-1} yr^{-1}, which, with the alkalinity change (a total of +7.9 μeq L^{-1} yr^{-1}), closely balances the change in acid anions. The concentration of reactive silica increased significantly at PC1-08, by 120 μg L^{-1} yr^{-1} or 4.3 μmole L^{-1} yr^{-1}; no such increase was observed at Hubbard Brook in response to the reduced acid input.

Two other observed changes validate those reported above. First, conductivity decreased by 1.75 μS yr^{-1}, as expected because of the SO_4^{2-} and base cation changes. Secondly, dissolved inorganic carbon (DIC) in the streamwater increased as less bicarbonate was lost via protonation and CO_2 degassing; this is consistent with the change in pH.

The changes in the chemistry of the stream measured at the base of the catchment (i.e. below the wetland area at station PC1) were very different from those observed in the upland drainage water. There was no change in alkalinity, pH or aluminum to balance the decrease in SO_4 (-5.9 $\mu eq\ L^{-1}\ yr^{-1}$) which was almost identical in magnitude to that of PC1-08. Cl (-1.1 $\mu eq\ L^{-1}\ yr^{-1}$) declined, so the total change in acid anions was 7.0 $\mu eq\ L^{-1}\ yr^{-1}$ (Table 3). This was almost entirely balanced by a decrease in base cations (-5.8 $\mu eq\ L^{-1}\ yr^{-1}$); at PC1-08 there was no change in base cations. DIC decreased, but only by 6% as much as at PC1-08, while neither DOC nor Si changed.

The chemistry of the water draining the upland part of the catchment responded to decreasing SO_4^{2-} levels in deposition with a decrease in SO_4^{2-} and inorganic monomeric aluminum, and an increase in alkalinity and pH. Similar results were reported for a small, experimentally-manipulated catchment (Risdalsheia, southern Norway) (Wright 1988). Base cation levels did not change. These changes can be considered improvements in water quality. If 1983 is considered to be the time at which changes in deposition chemistry stopped, then changes at PC1-08 continued on for an additional four years. These improvements were underway at the start of the sampling at this site; thus, we cannot estimate the lag time between decreasing SO_4^{2-} deposition and response at the upland site. In contrast to the upland drainage, the changes in stream chemistry observed below the wetland area (at PC1) do not indicate an improvement in water quality. The decrease in SO_4^{2-} was offset by a drop in base cations with no increase in pH or alkalinity. These changes, too, continued for about four years after changes in deposition chemistry stopped. As a result, Plastic Lake has been supplied with a more or less constant loading of acid, an amount which apparently has been enough to acidify the lake. The fact that

the lake's SO_4^{2-} concentration did not change significantly is partly an effect of the relatively long response time expected for the lake (the water replenishment time is approximately three years), and the fact that SO_4^{2-} concentration at PC1 was not as strongly correlated with time as evidenced by the fact that there were no statistically significant changes until the final year's data were included.

These results demonstrate that, although chemical recovery following reduction of S deposition was rapid in a stream draining only upland soils, the wetland portion of the Plastic Lake catchment has had a very substantial effect on the recovery process; the decreasing input of strong acid to the catchment and to the wetland resulted in a decreasing output of base cations from the wetland to the lake, but not a decline in strong acids. Organic acids have not been affected. Of a set of 24 catchments in our study area that we have studied over the past decade, 23 include wetland areas that affect stream drainage; this is probably a typical proportion for the area in eastern Canada affected by acidic deposition. The length of time that recovery is delayed by these wetlands is obviously of critical concern.

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Table 1. Initial concentration (average of first 6 months) and rate of change of chemical parameters (μeq L^{-1} yr^{-1} except pH or unless specified otherwise) at station PC1-08, an upland site above all wetland areas in catchment PC1. Results are based on linear regression analysis of monthly average concentrations vs. month number for the period November 1982 - December 1987. Between 1 and 14 samples per month were collected depending on flow volume. C_b is the sum of base cations (= Ca^{2+} + Mg^{2+} + Na^+ + K^+), s.e. is standard error, r is correlation coefficient, p (probability of r) is denoted as: $p < 0.05$ = *, $p < 0.001$ = **, $p < 0.00001$ = ***, NS = not significant. Al and F concentrations are totals of all chemical species.

Parameter	Initial Value	Annual Change	s.e.	r
Alkalinity	- 7.1	+ 4.6		0.7
0.68***				
pH	4.82	+0.047		0.007
0.69***				
Ca^{2+}	104	NS	-	0.17
Mg^{2+}	35.2	NS	-	0.06
Na^+	21.2	+ 0.6	0.3	0.32*
K^+	3.3	NS	-	0.12
C_b	164	NS	-	0.07
SO_4^{2-}	186	- 6.3	1.5	0.53**
Cl^-	9.3	- 1.0	0.4	0.33*
Al ($\mu g\ L^{-1}\ yr^{-1}$)	456	- 45.2	7.1	0.68***
F	4.7	- 0.31	0.05	0.68***
Cond ($\mu S\ yr^{-1}$)	32.3	- 1.75	0.2	0.76***
DOC ($mg\ L^{-1}\ yr^{-1}$)	1.8	NS	-	0.12
Si ($mg\ L^{-1}\ yr^{-1}$)	2.48	+ 0.12		0.03057**
DIC ($mg\ L^{-1}\ yr^{-1}$)	3.1	+ 0.8	0.17	0.57**

Table 2. Initial concentration (average of first 6 months) and rate of change of chemical parameters (μeq L^{-1} yr^{-1} except pH or unless otherwise specified) in main inflow to Plastic Lake (PC1). Results are based on linear regression analysis of monthly average concentrations vs. month number for the period May 1979 to December 1987. Between 1 and 119 samples per month were collected depending on flow volume. C_b is the sum of base cations (= Ca^{2+} + Mg^{2+} + Na^+ + K^+), s.e. is standard error, r is correlation coefficient, p (probability of r) is denoted as: $p < 0.05$ = *, $p < 0.001$ = **, $p < 0.00001$ = ***, NS = not significant. Al and F concentrations are totals of all chemical species.

Parameter	Initial Value	Annual Change	s.e.	r
Alkalinity	-15.3	NS	-	0.02
pH	4.38	NS	-	0.08
Ca^{2+}	114	- 3.2	1.0	0.33**
Mg^{2+}	38.7	- 1.4	0.4	0.34**
Na^+	27.6	- 0.65		0.2 035**
K^+	8.5	- 0.5	0.1	0.42**
C_b	189	- 5.8	1.4	0.39**
SO_4^{2-}	138	- 5.9	3.0	0.22*
Cl^-	19	- 1.1	0.4	0.28*
Al ($\mu g\ L^{-1}\ yr^{-1}$)	308	NS		- 0.07
F	3.6	NS		- 0.18
Cond ($\mu S\ yr^{-1}$)	29.0	0.6	0.3	0.18
DOC ($mg\ L^{-1}\ yr^{-1}$)	21.2	NS	-	0.14
Si ($mg\ L^{-1}\ yr^{-1}$)	2.13	NS	-	0.12
DIC ($mg\ L^{-1}\ yr^{-1}$) 0.38**	0.46	0.047		0.012

Table 3. Summary of chemical changes in the stream above (PC1-08) and below (PC1) the wetland area in the Plastic Lake catchment. All parameters expressed as μeq L^{-1} yr^{-1}. C_b is total base cations.

PC1-08			
Alkalinity	+4.6	C_b	0
SO_4^{2-}	- 6.3	Al^{n+}	- 3.3[1]
Cl^-	- 1.0		
A	0		
	- 2.7		- 3.3
PC1			
Alkalinity	0	C_b	- 5.8
SO_4^{2-}	- 5.9	Al^{n+}	0
Cl^-	- 1.1		
A	0		
	- 7.0		- 5.8

[1] Change was -45 μg L^{-1} yr^{-1}; estimated in μeq L^{-1} yr^{-1} by assuming average charge of +2.

LIST OF FIGURES

Fig. 1 Map of Plastic Lake subcatchment 1 showing location of wetland areas and sampling stations.

Fig. 2 Monthly average concentrations of alkalinity, SO_4^{2-} and base cations (C_b) at (a) sites above all wetland influence (PC1-08) and (b) at the base of the catchment (PC1).

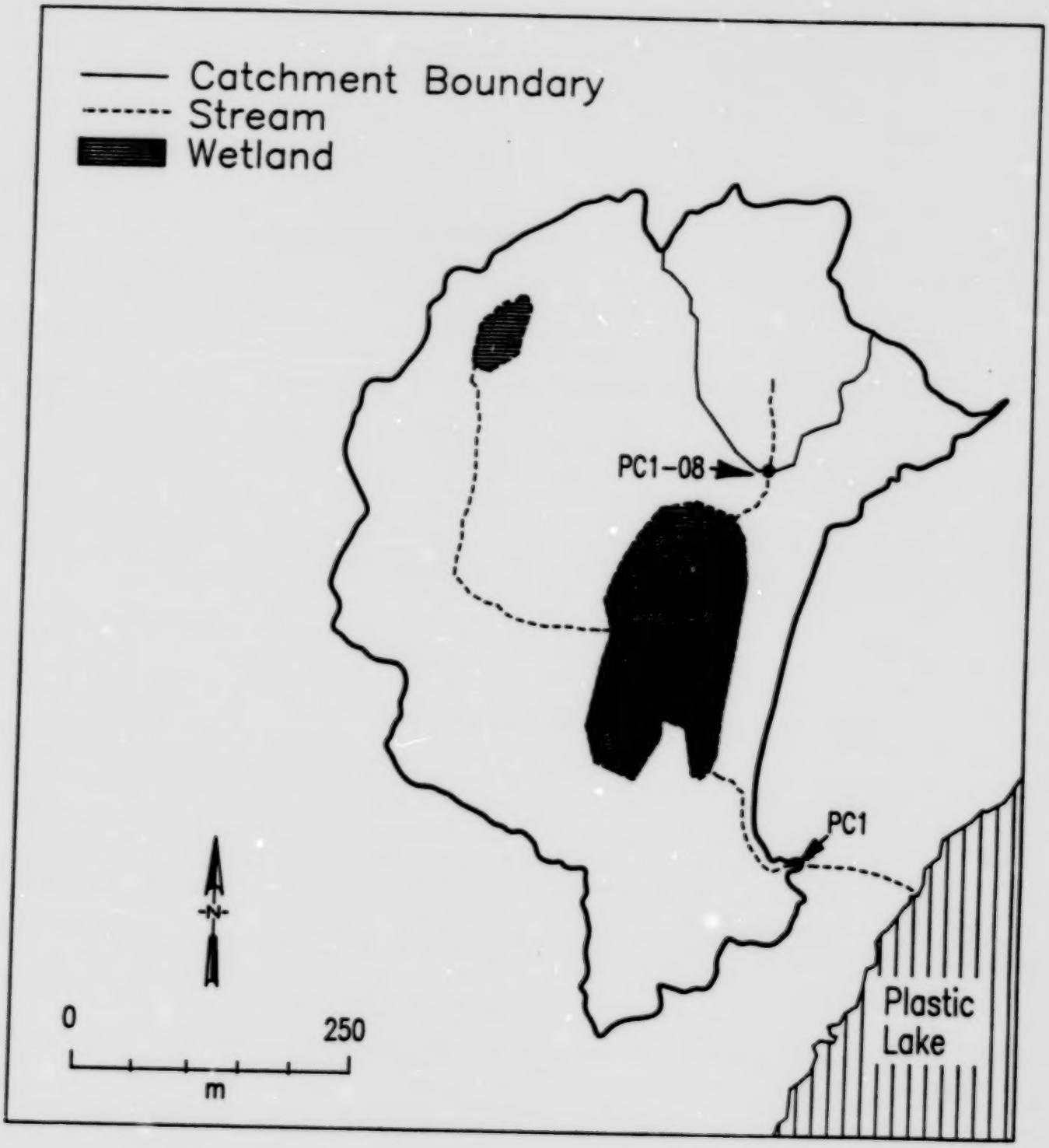
Catchment Boundary
Stream
Wetland
PC1-08
PC1
Plastic Lake
N
0
250
m

Fig. 1

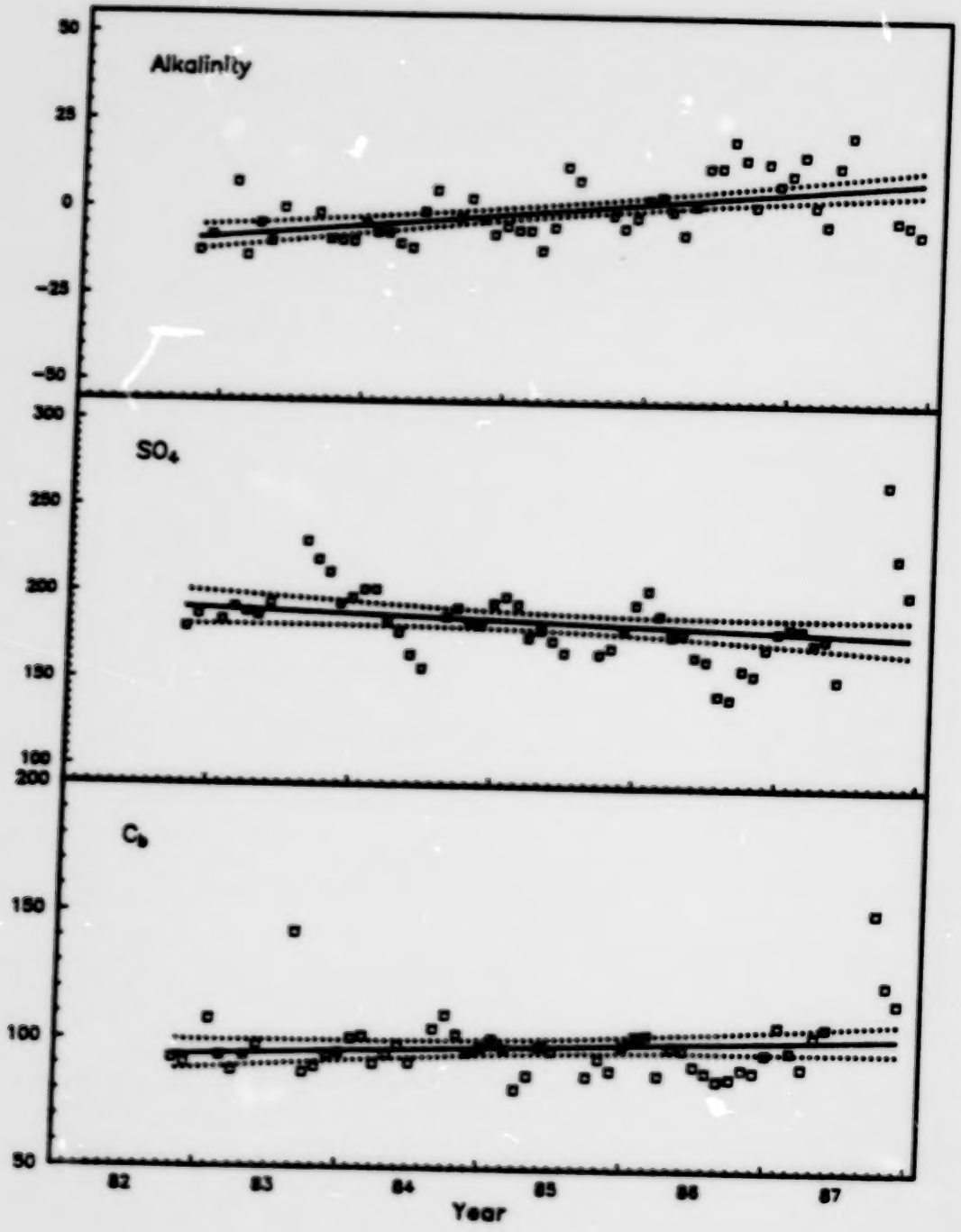
Alkalinity
50
25
0
-25
-50
SO_4
300
250
200
150
100
C_b
200
150
100
50
82
83
84
85
86
87
Year

Fig. 2 (a)

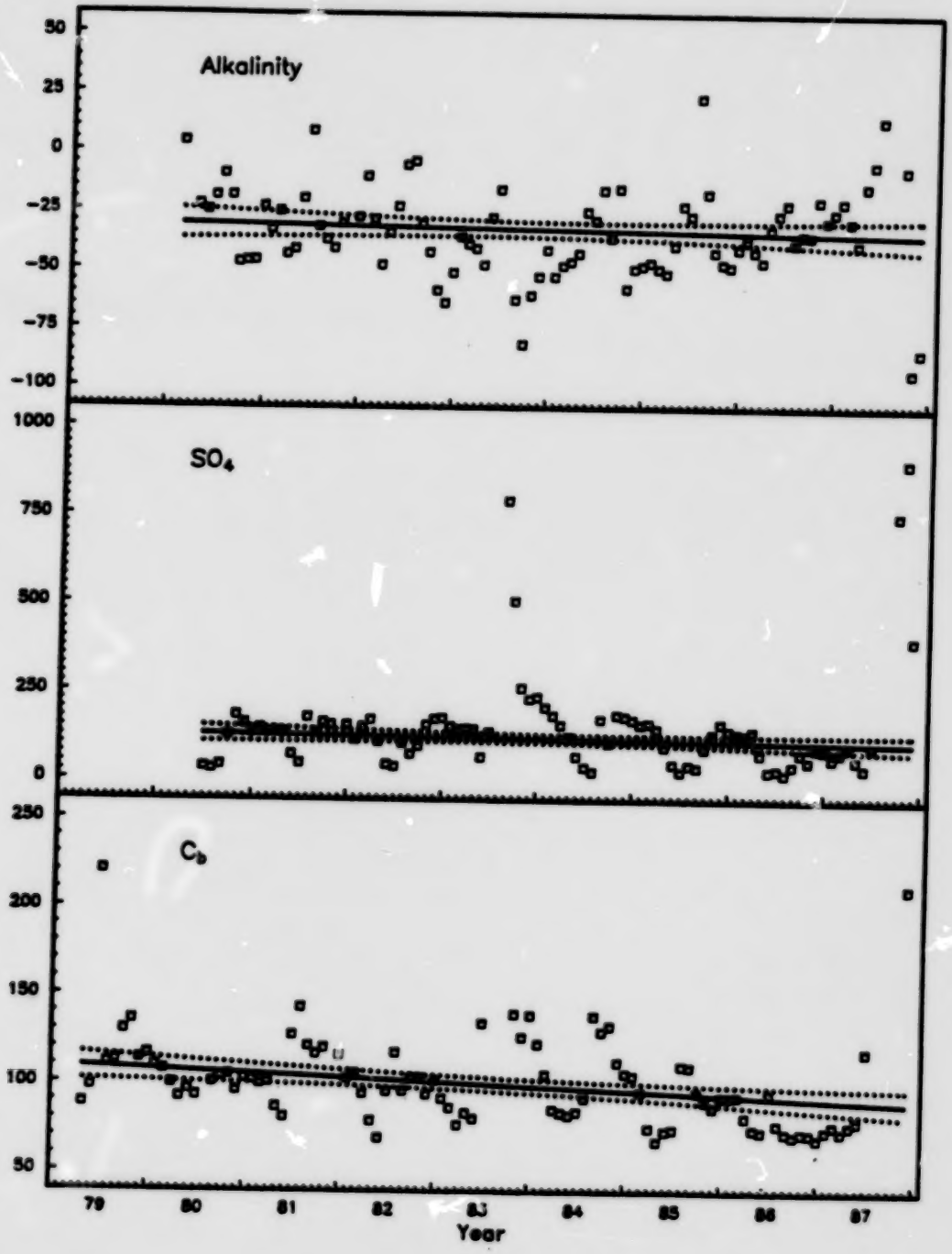
Alkalinity
50
25
0
−25
−50
−75
−100
SO4
1000
750
500
250
0
Cb
250
200
150
100
50
79
80
81
82
83
84
85
86
87
Year

Fig. 2 (b)